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Hafemeister, D.; de Waard, H.

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With constant ν_p, σ decreases as the ratio ω_p/ω becomes small, and it also exhibits oscillatory behavior. Equation (11) is used for general calculations. Macroscopic quantities only appear in Eqs. (7), (11), and (12) as a result of the use of relationship (5).

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Observation of the amorphous-crystalline phase transition in the Ovonic semiconducting glass $Te_{81}Ge_{15}As_4$ by the Mössbauer effect in Te^{125} and I^{129}

D. Hafemeister* and H. deWaard
Natuurkundig Laboratorium, University of Groningen, Netherlands
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Mössbauer spectra obtained with absorbers of $Te_{81}^{125}Ge_{15}As_4$ and a $ZnTe^{125m}$ source indicate that tellurium atoms are in an environment similar to that in tellurium metal. These spectra as well as those obtained with sources of $Te_{81}^{129m}Ge_{15}As_4$ and a CuI^{129} absorber indicate that the amorphous phase has a higher charge asymmetry than the crystalline phase which is consistent with the concept of "dangling" chemical bonds. Because of the great difference in the I^{129} spectra of the amorphous and crystalline phases it appears of interest to investigate Ovonic devices prepared with Te^{129m} in order to see if voltage-dependent phenomena can be observed in the I^{129} Mössbauer spectra.

The application of amorphous semiconducting glasses to switching and memory circuit elements has stimulated a great deal of interest in the technological and theoretical solid-state properties of these compounds. Studies of these materials which *lack long-range order* have led to the concept of a "mobility gap"[1] as well as to the concept of a band gap in materials in which Bloch's theorem is invalid.[2] Because of the disorder and defects in these materials one would except localized levels to exist in the band gap, but the results of photoemission experiments contradict each other[3,4] at present as to the existence of such levels. The switching mechanism in these devices has been discussed in terms of recrystallization after electrical heating and capacitive discharge[5] (a long-range effect) and in terms of the removal of "dangling" chemical bonds (a short-range effect). At higher voltages a discharge probably creates ordered "filaments" of crystallized material without dangling chemical bonds and with a relatively higher conductivity.

With the Mössbauer effect we may study the problem of short-range order and of "dangling" chemical bonds in the amorphous state. The Mössbauer effect is suited for observing changes in the local environment of the atoms of an amorphous semiconducting material when it is transformed into the crystalline state because of its relatively broad line width (in contrast to NMR) which will allow measurements in disordered materials. In the present work the Mössbauer effect has been exploited to observe such changes in Mössbauer spectra obtained with Ovonic absorbers enriched in Te^{125} as well as with sources prepared with radioactive Te^{129m} which decays to I^{129}.

For our experiments we have used $Te_{81}Ge_{15}As_4$ which has been shown by Ovshinsky[6] to display memory-type switching in thin-film form. In the initial stages of the experiment Te^{129m} sources were prepared by implanting Te^{129m} with an isotope separator into $Te_{81}Ge_{15}As_4$ and also by reactor irradiation of $Te_{81}^{128}Ge_{15}As_4$. The spectra obtained from these two types of sources were very smeared, undoubtedly due to extensive radiation damage. In order to avoid the radiation-damage effects we next used absorbers enriched to 65.5% in Te^{125} and sources

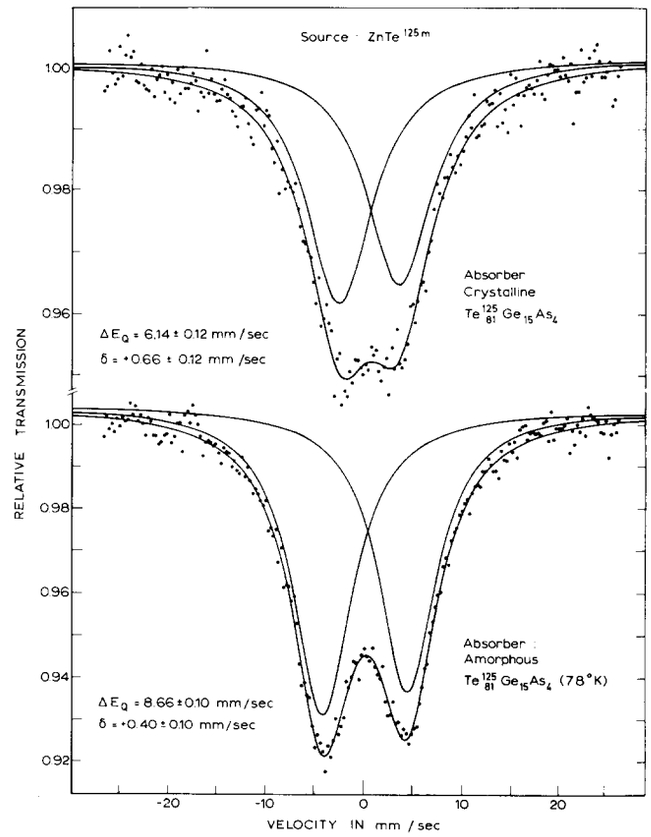

FIG. 1. Mössbauer spectra of the 35.6-keV γ ray of Te^{125} transmitted from a $ZnTe^{125m}$ source through $Te_{81}^{125}Ge_{15}As_4$ absorbers in the amorphous and crystalline phases.

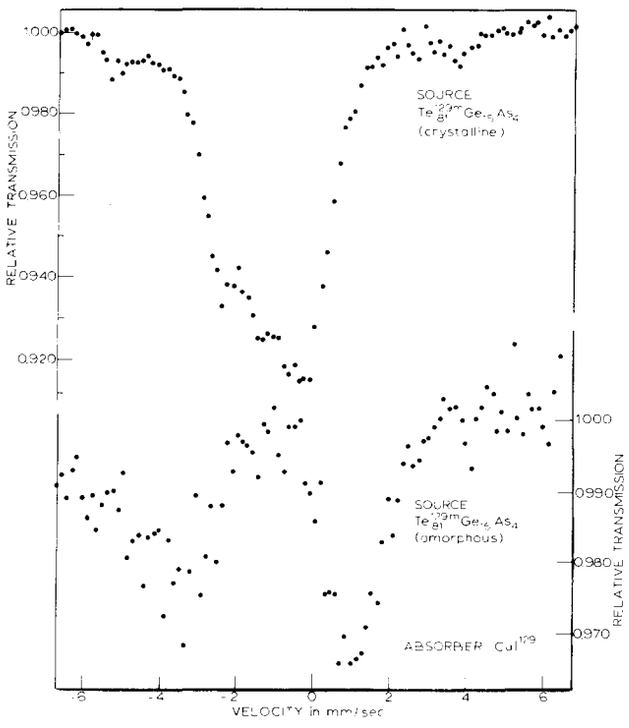

FIG. 2. Mössbauer spectra of the 27.7-keV γ ray of I^{129} using sources of $Te_{81}^{129m}Ge_{15}As_4$ in the amorphous and crystalline phases and a CuI^{129} absorber.

prepared with radioactive Te^{129m}. The Te^{125}-enriched materials were prepared by the Energy Conversion Devices Corp. of Troy, Mich., and the Te^{129m} sources were prepared in Groningen.

Spectra taken at 78 °K with a single-line $ZnTe^{125m}$ source and with absorbers in the amorphous and crystalline phases are shown in Fig. 1. The amorphous materials were converted into the crystalline state by heating at 275 °C for 1 h. The crystalline and amorphous states were identified from Debye-Scherrer patterns. The Mössbauer spectrum of *amorphous* material displays two distinct peaks with intensity ratio (1.1 ± 0.1) which can be interpreted for the Te^{125} 1/2 to 3/2 nuclear transition in terms of a quadrupole splitting $\Delta E_Q = 8.66 \pm 0.10$ mm/sec and an isomer shift $\delta = +0.40 \pm 0.10$ mm/sec. The linewidths were determined to be 7.53 ± 0.16 and 7.21 ± 0.17 mm/sec, which is 40% broader than twice the natural linewidth of 5.21 mm/sec. This broadening can be accounted for by the thickness of the absorber. For the *crystalline* state (Fig. 1) the spectrum can again be explained by quadrupolar splitting, but with a 30% *smaller* value of the quadrupolar splitting $\Delta E_Q = 6.14 \pm 0.12$ and $\delta = +0.66 \pm 0.12$ mm/sec.

These results for ΔE_Q of Te^{125} in amorphous and crystalline $Te_{81}Ge_{15}As_4$ are quite similar to those obtained by other workers on amorphous and crystalline tellurium. Boolchand, Robinson, and Jha[7] obtained $\Delta E_Q = 7.74 \pm 0.10$ mm/sec for metallic tellurium at 4 °K which when corrected[8] to 78 °K would be about 7.5 mm/sec. Our values for the isomer shift in the two phases are also quite similar to the shift of tellurium reported by Ruby and Shenoy,[9] $\delta = +0.57 \pm 0.06$ mm/sec with respect to a $ZnTe^{125m}$ source. Similar increases in ΔE_Q have been observed[10,11] when $AuTe_2^{125}$ and Cu_3Au^{197} are transformed from the ordered to the disordered state. The spectra[10] of amorphous systems such as $Te_{70}^{125}Cu_{25}Au_5$ are also quite similar to those displayed in Fig. 1.

Somewhat similar results to our Mössbauer measurements have been obtained by Senturia *et al.*[12,13] who have performed NMR measurements on Te^{125} in the conducting and nonconducting states of the same Ovonic, $Te_{81}Ge_{15}As_4$. Their measurements indicate that the chemical shift of the conducting-crystalline phase has the same value as that of crystalline tellurium indicating that the Te^{125} resides in sites quite similar to those in crystalline tellurium. In addition they have observed a difference in the chemical shift, $\sigma = \Delta H/H$, of 1×10^{-3} between the two phases. This chemical shift difference indicates a substantial structural difference between the crystalline and the amorphous phases, analogous to our results on the quadrupole splitting of the Mössbauer spectra.

The spectra shown in Fig. 2 were obtained with sources of $Te_{81}Ge_{15}As_4$ prepared with the isotope Te^{129m} which emits upon decay the 27.7-keV γ ray of I^{129}. These spectra show a very dramatic change when transforming from the amorphous to the crystalline state. As in the case of the Te^{125} data, the spectra of the amorphous phase displays a larger quadrupole interaction than the crystalline phase. A numerical interpretation of the data is complicated by the larger number of lines of this 5/2 to 7/2 transition as well as the possibility of more than one type of site.

From the above data we may conclude the following:

(i) The Mössbauer parameters ΔE_Q and δ for the Te^{125} in the crystalline Ovonic compound $Te_{81}Ge_{15}As_4$ are very similar to those obtained for crystalline tellurium. Similarly NMR measurements[12,13] of the chemical shift of Te^{125} also indicate that Te^{125} resides in sites which are very similar to those in crystalline tellurium.

(ii) Both the Te^{125} and I^{129} data indicate that the amorphous state has a larger quadrupole splitting than the crystalline state. The difference in the chemical shifts observed between the two phases[12,13] also gives evidence of a markedly different chemical bonding. This probably indicates that the "dangling" chemical bonds give a distortion of the change distribution which is decreased when the bonds are filled in the crystalline state.

(iii) Because of the large differences in the I^{129} spectra it may be possible to observe differences in the Mössbauer spectra when a voltage is applied. Ovshinsky[6] has shown that application of electric fields of about 10^4 V/cm will recrystallize some of the amorphous material into highly conductive filaments. Using Ovshinsky's values for the diameters of the filaments (5×10^{-5} cm) and the areas of his devices (10^{-4} cm^2) as well as the great differences observed in Fig. 2, it seems attractive to explore the switching mechanism by Mössbauer measurements.

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*Present Address: California Polytechnic State University, San Luis Obispo, Calif. 93401.
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Zero temperature sensitivity of bubble diameter*

Magid Y. Dimyan and Edward Della Torre
Department of Electrical Engineering and Communications Research Laboratory, McMaster University, Hamilton, Ontario, Canada

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The condition for zero temperature sensitivity of bubble diameter in some uniaxial magnetic materials is obtained in terms of the material parameters. The ratio of the fractional changes in wall energy density and saturation magnetization which gives zero temperature sensitivity of bubble diameter is plotted as a function of plate thickness and bubble diameter. The resulting curves can be used in designing bubble devices having fixed bubble sizes.

The temperature sensitivities of bubble diameter in two types of uniaxial magnetic materials have previously been derived in terms of the material parameters.[1] It was shown that for materials whose temperature dependence is mainly due to wall energy variation, such as orthoferrites and especially the mixed rare-earth orthoferrites, the temperature sensitivity of bubble diameter is given by

$$S_\sigma = \frac{\rho_0}{\sigma_w}\frac{\Delta\sigma_w}{\Delta T}, \tag{1}$$

where

$$\rho_\sigma = \frac{\sigma_w}{d}\frac{\Delta d}{\Delta\sigma_w} = \frac{l_M/h}{S_0(a) - l_M/h}, \tag{2}$$

σ_w is the wall energy density per unit area. $\Delta\sigma_w/\sigma_w$ is the fractional change in wall energy density, ΔT is the change in temperature, d is the bubble diameter, h is the plate thickness (assumed uniform), $a = d/h$ is the bubble aspect ratio, $l_M = \sigma_w/4\pi M_s^2$ is the material characteristic length, M_s is the saturation magnetization, and $S_0(a)$ is the radial stability function defined by Thiele.[2,3] On the other hand, for materials whose temperature dependence is mainly due to magnetization variation such as in some uniaxial garnets, the temperature sensitivity of bubble diameter is

$$S_M = \frac{\rho_g}{M_s}\frac{\Delta M_s}{\Delta T}, \tag{3}$$

where

$$\rho_M = \frac{M_s}{d}\frac{\Delta d}{\Delta M_s} = \frac{F(a) + l_M/h}{S_0(a) - l_M/h}, \tag{4}$$

$\Delta M_s/M_s$ is the fractional change in magnetization, and $F(a)$ is the magnetostatic force function.

Thus, it can be seen from Eqs. (2) and (4) that for uniaxial materials whose wall energy densities as well as magnetizations vary in the same direction with temperature, the absolute value of the total change in bubble diameter for a fixed bias field will be

$$\frac{|\Delta d|}{d} = \left|\rho_0\frac{\Delta\sigma_w}{\sigma_w} - \rho_g\frac{\Delta M_s}{M_s}\right| \tag{5a}$$

$$= \left|\frac{l_M/h}{S_0(a) - l_M/h}\frac{\Delta\sigma_w}{\sigma_w} - \frac{F(a) + l_M/h}{S_0(a) - l_M/h}\frac{\Delta M_s}{M_s}\right|. \tag{5b}$$

Smith and Anderson[4] showed that for l_M to be temperature independent

$$\Delta\sigma_w/\sigma_w = 2\Delta M_s/M_s. \tag{6}$$

Even if l_M is temperature independent the bubble diameter will vary with temperature due to the change in magnetization. It can be seen from Eq. (5b) that the condition for zero temperature sensitivity of bubble diameter for a fixed bias field is given by

$$\frac{\Delta\sigma_w/\sigma_w}{\Delta M_s/M_s} = 1 + \frac{hF(a)}{l_M}. \tag{7}$$

Noting that $F(a)$ is given by[2,3]

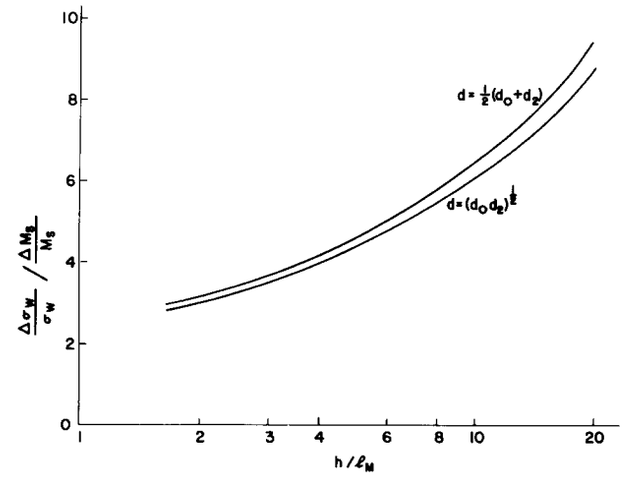

FIG. 1. The ratio of the fractional changes in wall energy density and magnetization for zero temperature sensitivity as a function of plate thickness for two bias conditions.